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Deactivation of organosulfonic acid functionalized silica catalysts during biodiesel synthesis

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ABSTRACT

The reusability of silica functionalized with 4-ethyl-benzene sulfonic acid groups used as catalyst in biodiesel production from sunflower oil/methanol mixtures has been investigated. This material was used for four runs under batch mode operation, at different reaction temperatures (373, 423 and 473 K), with a catalyst loading of 1.5 wt.% referred to oil and with a methanol/oil molar ratio equal to 6. The catalyst is significantly deactivated during the first run, while the activity for the second and successive runs are very similar.

Fresh and used catalysts were characterized by chemical analysis, N_2 adsorption–desorption isotherms, infrared spectroscopy and evolved gas analysis by mass spectrometry. Leaching of the organosulfonic groups and adsorption of organic compounds onto the acid sites was detected in the used catalysts. Reactants and products are involved in the leaching process, although glycerine has the highest leaching capacity. The organic deposits are formed by side reactions involving reactants and/or products. The solid porous structure remained unchanged after catalyst use, indicating that sintering or other alterations of the porous network can be discarded as source of deactivation. Leaching and deposition effects occur predominantly during the first run, slowing down notably in subsequent cycles. Both leaching and organic deposits participate of the deactivation; the latter increases its impact at reaction temperatures higher than 423 K.

Partial catalyst regeneration by removal of the organic adsorbates could not be achieved by treatment at high temperature because the deposits and the organosulfonic acid sites were combusted simultaneously.

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1. Introduction

Biodiesel utilization as substitute of petroleum-derived diesel fuel has experienced a remarkable growth during the last years in USA, EU, and other developed countries. Some advantages derived of biodiesel use include biodegradability, non-toxicity, renewable character, and lower pollutant emissions [1–3]. Biodiesel consists of a mixture of fatty acid methyl esters (FAME) obtained via transesterification of triglycerides with methanol (methanolysis). The final cost of biodiesel, more expensive than petroleum-derived diesel, depends markedly on the feedstock price. The use of inexpensive sources (crude oils, frying oils, poultry fat or yellow grasses) appears as an attractive option because it would result in a significant reduction of the final price of biodiesel [4–7].

Inexpensive raw feedstocks contain typically high concentrations (>0.5 wt.%) of free fatty acids (FFA) and water. Hence, base catalysts are not suitable because of the inevitable saponification reaction between catalyst and FFA to form soaps, which consumes the catalyst and requires expensive separation steps downstream to purify the biodiesel. Moreover, water impurities present in the triglycerides feedstock may hydrolyze the methyl esters previously formed in the transesterification reaction, decreasing thus the yield to biodiesel [4]. These problems can be overcome by refining the low-quality oils, although this leads to higher final costs.

In this context, the use of acid catalysts solves the drawbacks associated with the use of inexpensive sources for triglycerides. Esterification of FFA and transesterification of triglycerides can be performed simultaneously. Acid transesterification catalysis requires, however, higher reaction temperature and pressure to achieve rates comparable to those obtained with base catalysts. Homogeneous acid catalysts (H_2SO_4, HCl, etc.) are commonly proposed for these reactions, but their use leads to other drawbacks, as a difficult and costly neutralization step is required, and important safety and corrosion-related problems associated to the use of strong liquid acids appear. The development of solid acid catalysts (reusable and easy to separate from the reaction mixture) for the transesterification of inexpensive triglycerides can cope with these aforementioned problems. Many solid acid catalysts

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have shown promising results in FFA esterification and triglycerides transesterification reactions [4,8,9]. Special emphasis has been devoted to those catalysts containing sulfonic groups. Thus, sulfated-zirconia [10], sulfonated sugar-derived carbon [11–14] and silica solids functionalized with organosulfonic groups [15,16] have been proved to be very active at moderate temperatures and pressures (333–473 K and methanol autogenous pressure).

Leaching of sulfonic or sulfuric acid species can limit, however, the reusability of these families of catalysts [10,12,17]. The leached species are also partially responsible of the overall catalytic activity observed with these systems. Although the leaching of active species has been detected in the case of organosulfonic functionalized silica catalysts [15], investigations devoted to the understanding of these processes are not common in the literature. Moreover, the deposits of organic species as a relevant cause of catalyst deactivation has been scarcely considered in these families of solid catalysts mentioned above. Fouling or poisoning of the acid sites by deposits of organic molecules is a very plausible possibility in the case of transesterification by acid catalysts. Indeed, coke deposition has been detected in biodiesel isomerization reactions on acid catalysts [18]. Methanol and glycerine can also form coke deposits on acid catalysts [19,20]. To our knowledge, the origin and nature of these organic species, as well as the interaction with the surface acid sites and the possibility of removing these species by thermal or chemical treatments have not been addressed in the case of the biodiesel reaction catalyzed by acid sites.

Due to the above mentioned reasons, we have investigated the leaching of active species and whether the building-up of organic products derived from secondary reactions involving reactants and/or products can cause the deactivation of silica functionalized catalysts. We have first observed the deactivation of a commercial functionalized silica by conducting the transesterification reaction at different temperatures. The fresh and used catalysts were then characterized by chemical analysis, N_2 adsorption isotherm, diffuse reflectance infrared Fourier transform (DRIFT) studies, and evolved gas analysis by mass spectrometry (EGA-MS) to gain information about the likely mechanism of deactivation, especially focusing on the leaching of sulfur species and the deposits of organic species. The evaluation of the individual contribution (leaching of active species or the formation of deposits) to the overall deactivation is also carried out through the discussion of these characterization results. The research was also extended to test whether the deactivated catalyst could be reactivated by thermal regeneration by combusting the organic deposits.

2. Experimental

2.1. Catalyst preparation and pretreatment

A commercial silica functionalized with 4-ethyl-benzene sulfonic groups was obtained from SiliCycle® Inc. (Canada). Supplier specifications indicate 40–63 μm particle size. Thermogravimetric analysis (TGA) in N_2 reveals that physisorbed water is removed at 373 K. Weight loss due to the decomposition of the functional groups occurs at temperatures higher than 673 K. Hence, the solid was outgassed at 473 K for 12 h before measuring the catalytic properties.

2.2. Catalysts characterization

Fresh and used catalysts were washed by stirring at room temperature with 50 mL of *n*-heptane (*ca.* 14 mL g_{cat}^{-1}, >99.5%, Fluka) and then with 50 mL of methanol (*ca.* 14 mL g_{cat}^{-1}, 99.8%, <0.005% H_2O, Scharlau). Methanol is a reactant and *n*-heptane was selected as a volatile solvent with similar hydrophobicity to sunflower oil. In this way, only the heaviest and/or strongly chemisorbed molecules that may be involved in the catalyst deactivation would remain on the surface after these rinsing steps. Other molecules that may be filling the pores or weakly adsorbed over the surface are rinsed by these treatments. These latter molecules cannot be involved in the deactivation as they must also be rinsed by the methanol and the triglycerides present in the initial reaction mixture. The solids were subsequently dried at 353 K for 12 h to remove potential residues of *n*-heptane and methanol before conducting the characterization studies.

In addition, the fresh sample (1 g) was independently treated with 120 mL of sunflower oil, methanol, biodiesel, and glycerine at 423 K for 5 h to gain information about the individual contribution of each compound on the leaching and/or deposition of organic species. These treated samples were successively rinsed with *n*-heptane and methanol as indicated above. The biodiesel required for this treatment was previously obtained by methanolysis of sunflower oil catalyzed by KOH (1 wt.%, 333 K, 2 h and molar methanol/oil ratio = 14). The biodiesel phase was rinsed with HCl and CH_2Cl_2 as explained elsewhere [21].

Characterization by N_2 adsorption–desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2010 gas adsorption analyzer. The rinsed samples were previously evacuated under vacuum at 393 K for 12 h. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation and the mean pore diameter was obtained by applying the Barret–Joyner–Halenda (BJH) method on the desorption branch.

The elemental analysis of the solids was performed on a LECO CHNS-932 analyzer. Typically, 1 mg of sample was placed in an Ag vial and combusted at 1333 K under pure O_2 atmosphere. The CO_2, H_2O and SO_2 gases were quantified by Fourier transform infrared (FT-IR) spectroscopy, while N_2 was determined by differential thermal conductivity.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained with a Nicolet 5700 FT spectrophotometer equipped with an *in situ* chamber, a diffuse praying mantis and a high sensitivity Hg–Cd–Te detector. Spectra were obtained at a resolution of 4 cm^{-1} with an accumulation of 128 scans. Typically, the finely grounded samples (*ca.* 50 mg) were placed in the cup of the *in situ* DRIFT chamber. With the intention of removing any trace of methanol, *n*-heptane and water adsorbed over the surface, the sample was pretreated under Ar flow (*ca.* 50 mL min^{-1}) at 423 K for 30 min before collecting the infrared spectra also at 423 K.

Evolved gas analysis by mass spectrometry (EGA-MS) was performed by loading the washed samples (*ca.* 100 mg) in a U-shaped quartz reactor connected to a Balzer Prisma™ quadrupole mass spectrometer (QMS 200). The analysis was conducted while flowing a O_2/Ar mixture (50 mL min^{-1}, 20 vol.% O_2) from room temperature to 1100 K at a heating rate of 10 K min^{-1}. The fragments m/z = 18 (H_2O^+), 28 (CO^+), 44 (CO_2^+) and 64 (SO_2^+) were continuously monitored with the mass spectrometer. Gas lines from the reactor outlet to the MS inlet were heated to 393 K to avoid water condensation.

2.3. Catalytic experiments

The transesterification reaction of commercial sunflower oil with methanol was carried out in a 500 mL Autoclave Bolted Closure reactor of Autoclave Engineers with a magnedrive agitator. The reaction temperature was adjusted with a thermostatically controlled heating jacket. Initially, the reactor was loaded with sunflower oil (260 g, commercial), methanol (56 g, 99.8%, <0.005% H_2O, Scharlau), and the dried catalyst (4 g). The temperature was then increased up to the desired value (373–473 K), once the temperature is reached the agitation (800 rpm) starts. This is considered the beginning of the reaction. Catalytic reactions were conducted at the autogenous pressure. Aliquots (2 mL) were

periodically taken from the reaction mixture at different reaction times through the exit located at the bottom of the vessel (the liquid is driven out by the help of the autogenous pressure). A 2 μm filter prevented the removal of the catalyst particles. The aliquots were washed twice with water and CH_2Cl_2. The alcoholic phase (glycerine, H_2O, CH_3OH) was separated from the ester phase (glycerides, methyl esters, CH_2Cl_2) by decantation. The residual dichloromethane was removed from the methyl esters by evaporation in ambient air at 353 K. Briefly, the FAME content was determined in accordance with the European regulated procedure EN 14103 using a gas chromatograph (Agilent 6890GC) connected to a flame ionization detector (FID). Further details of the analysis are given elsewhere [21–23].

3. Results and discussion

3.1. Sunflower oil transesterification with methanol

Fig. 1 depicts the yield to FAME as a function of reaction time obtained in sunflower oil transesterification with methanol at 423 K. In the first run, the FAME yield reaches *ca.* 60% after 300 min of reaction time. Higher yield values have been previously reported in the literature at similar reaction conditions, indicating that chemical equilibrium is not limiting the yield measured in our work [15,21–23]. Negligible formation of FAME (<0.5%) was observed in a blank transesterification reaction experiment (no catalyst), excluding thus the potential contribution from non-catalytic reactions under this operation conditions.

The acid functionalized silica catalyst was reutilized several times following a series of four successive 5-h runs at 423 K (Fig. 1). Experimentally, the reaction mixture was cooled down and withdrawn from the reactor after each catalytic cycle. A new batch of sunflower oil and methanol were then loaded for a subsequent reaction cycle. The catalyst suffers a remarkable deactivation during the first run, while the reaction rate of second, third and fourth cycles are rather similar, especially for the last two (Fig. 1). This means that the rate of deactivation slows down significantly after the first run.

Fig. 2 depicts the rate of FAME formation for the different runs at 373, 423 and 473 K after 15 min of reaction. The reaction rate derived from the yields at 15 min corresponds to differential values of the reaction rate. Yield of a blank experiment at 373 and 423 K

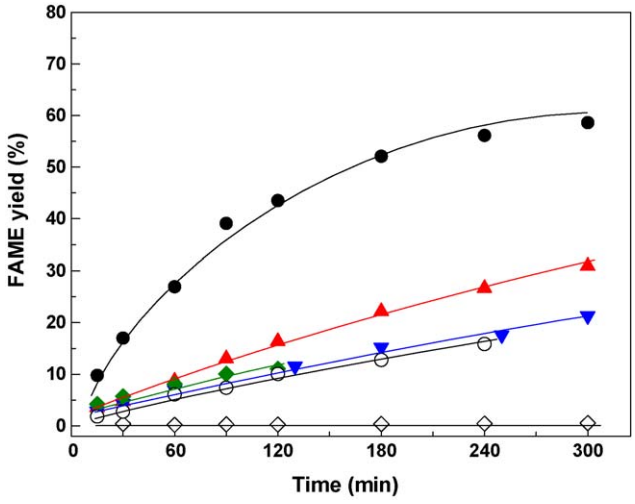

Fig. 1. FAME yield with silica functionalized with 4-ethyl-benzene sulfonic groups in sunflower oil transesterification with methanol at 423 K, 800 rpm, methanol/oil molar ratio of 6, and 1.5 wt.% catalyst referred to the oil (symbols: (●) first run; (▲) second run; (▼) third run; (◆) fourth run; (◇) blank experiment; (○) leached species in methanol).

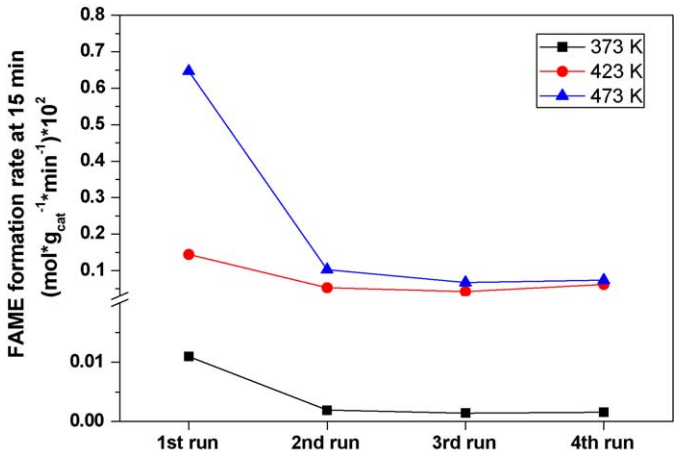

Fig. 2. Temperature effect on the FAME yield at 15 min shown by the silica functionalized with 4-ethyl-benzene sulfonic groups during 4 cycles in sunflower oil transesterification with methanol at 373 K (■), 423 K (▲) and 473 K (●) (800 rpm, methanol/oil molar ratio of 6, and 1.5 wt.% catalyst referred to the oil).

was negligible, whereas reached *ca.* 5% at 473 K. The noncatalytic contribution was then subtracted to convey information only of the activity due to the solid. Catalyst deactivation occurs inevitably in the 373–473 K temperature range. The most significant differences in activity are observed between the first and second run. At a given reaction temperature the initial reaction rate of the second, third and fourth runs are very similar, which suggests that deactivation occurs mainly during the first contact with the reaction medium; that is, in the first run. Hereafter, deactivation proceeds at much lower rate.

The observed catalyst deactivation could be due to: (i) modification of the catalyst pore structure; (ii) leaching of active species; and/or (iii) deposition of organic species over the surface of the catalyst that can result in the fouling or poisoning of the active sites. Next, we will discuss the individual contribution of these effects into the overall deactivation process.

3.2. Catalyst pore structure

The catalyst recovered after the fourth run was rinsed as indicated in the experimental section and the N_2 adsorption–desorption isotherms were subsequently recorded to asses on the textural properties of the catalyst. The specific surface area and the mean pore diameter of the fresh and used catalysts after the fourth catalytic cycle are reported in Table 1. Irrespective of the reaction temperature, the specific area values and mean pore diameter of the used catalyst are similar (within 10% of experimental error) to that of the fresh catalyst. This clearly indicates that catalyst deactivation is not related to the modification of the porous structure either by sintering or by fouling of the surface by extensive deposition of organic species.

3.3. Evaluation of the leaching process by chemical analysis

The contribution of methanol-leached active species to the overall catalytic activity was also investigated. Experimentally, methanol was contacted with the fresh catalyst at 423 K and 800 rpm in the same reaction vessel used for conducting the catalytic tests. Then, methanol was filtrated through the 2 μm filter located at the bottom of the reactor and the catalyst removed out of the vessel. The filtrated methanol was again introduced in the vessel along with fresh sunflower oil at a methanol/oil molar ratio of 6 and reaction was performed at 423 K. The profile of FAME yield as a function of reaction time is shown in Fig. 1. Results

Table 1
Specific surface area and the mean pore diameter of the fresh and used catalysts after the fourth run at different reaction temperatures.

	Surface area ($m^2 g^{-1}$)	Mean pore diameter (nm)
Fresh catalyst	317	5.4
Used at 373 K after fourth run	304	5.8
Used at 423 K after fourth run	340	5.4
Used at 473 K after fourth run	302	5.0

Reaction conditions: methanol/oil = 6 (molar ratio), 1.4 wt.% catalyst referred to oil.

clearly indicate that: (i) leaching of active species occurs significantly in the reaction mixture, and (ii) the activity of these leached species is significant. The FAME yield obtained in this experiment is essentially identical to that corresponding to the third and fourth runs (Fig. 1). As we will show later, this is a coincidence and does not indicate that the activity in the third and fourth run is due to homogeneous species present in the reaction medium as a result of methanol leaching.

In an attempt to gain information on the leaching of the organosulfonic groups, elemental chemical analysis of the fresh and used catalysts after the fourth run was carried out (Table 2). The atomic C/S ratio of the fresh sample is 7.61, very close to the value derived from the stoichiometry of the functionalizing species (C/S = 8). This is an indication of the correctness of the chemical analysis. Table 2 also reveals that the sulfur content of the used catalysts (0.63–0.77 mmol S/g SiO_2) is noticeably smaller than that of the fresh sample. Therefore, we conclude that partial leaching of sulfonic species occurs. Moreover, large differences among the used catalysts were not found and even when used at 373 K, the leaching is important.

Table 2 also shows that the carbon content of the catalyst used at 373 K is lower than that of fresh sample. This evidences that the leaching process not only affects the sulfonic functionality, but also the hydrocarbon moiety. In contrast, the carbon content of the catalyst used at 473 K is significantly larger than those found for the fresh catalyst and catalyst used at 373 K, evidencing the deposition of carbon containing species. The presence of these deposits in the catalysts used at 373 and 423 K cannot be discarded because the measured carbon content is the combination of two opposite effects: leaching of the organosulfur entities and deposition of C-containing species. The chemical analysis does not allow us to determine the individual contribution of these two phenomena. Nevertheless, DRIFT experiments (discussed later) show that deposits are also present over the surface of the catalysts used at 373 and 423 K. DRIFT results will also show that the deposits have a hydrocarbonaceous nature.

Table 2 also summarizes elemental analysis of the catalyst subjected to different pretreatments with the pure reactants (methanol and oil) and products (glycerine and biodiesel) at 423 K for 5 h. Partial leaching of the sulfonic entities occurs with all

Table 2
Elemental analysis (sulfur and carbon) of the fresh, used catalysts (after fourth run) and fresh catalyst treated with pure methanol, glycerine, biodiesel and sunflower oil at 423 K for 5 h.[a].

	mmol S/g SiO_2	mmol C/g SiO_2
Fresh catalyst	0.94	7.15
Used at 373 K after fourth run	0.77	6.52
Used at 423 K after fourth run	0.63	7.25
Used at 473 K after fourth run	0.74	8.87
Fresh catalyst contacted with methanol	0.71	6.53
Fresh catalyst contacted with glycerine	0.39	12.11
Fresh catalyst contacted with biodiesel	0.81	12.54
Fresh catalyst contacted with sunflower oil	0.80	28.41

[a] The samples were previously washed with *n*-heptane and methanol to rinse the pores and to remove the weakly adsorbed species.

Table 3
Elemental analysis (sulfur and carbon) of the fresh and used catalyst after the first and successive runs at 423 and 473 K.[a].

	mmol S/g SiO_2	mmol C/g SiO_2
Fresh catalyst	0.94	7.15
First run at 423 K	0.63	7.10
Second run at 423 K	0.68	6.90
Third run at 423 K	0.65	6.97
Fourth run at 423 K	0.63	7.25
First run at 473 K	0.68	8.30
Second run at 473 K	0.71	8.95
Third run at 473 K	0.70	9.03
Fourth run at 473 K	0.74	8.87

[a] The samples were previously washed with heptane and methanol to rinse the pores and to remove the weakly adsorbed species.

reactants and products, although this process is more intense with glycerine. Concerning the deposition of C-containing species, the most significant deposition occurs when the catalyst is contacted with sunflower oil. Nevertheless, the treatment with either glycerine or biodiesel also results in a significant accumulation of deposits.

Table 3 reports on the sulfur and carbon content of the samples used at 423 and 473 K after the first, second, third, and fourth run. Experimentally, small portions of catalyst (~100 mg) were removed from the reactor after each cycle to thus conduct the characterization studies. The analysis of fresh catalyst is also included in Table 3 for comparison purposes. Differences in sulfur content are not significant among all the used catalysts, indicating that leaching of S-containing species takes place predominantly during the first run and that additional removal of these species does not occur in subsequent cycles. Consequently, we do not expect the presence of leached species in the third and fourth runs, being the activity due to the surface species (heterogeneous catalysis) instead of the leached species (homogeneous catalysis). Therefore, the identical catalytic activity of the third and fourth run compared to that observed with methanol-leached species is a mere coincidence. We must also bear in mind that glycerine is continuously formed during the course of the reaction, and this strongly increases the leaching capacity of the reaction medium. This means that the homogeneous contribution from the sulfonic leached species may become larger during the progress of the reaction in the first run. Concerning the C content, at 423 K is quite similar to that of fresh sample. It does not increase significantly after the first run. At 473 K, the values for the different runs are higher than that of the fresh sample because the deposition of C-containing species compensates the removal by leaching of the organosulfonic groups. The C content of the 473 K samples for the different runs are similar indicating that the accumulation of C-containing species slows down after the first cycle.

Summarizing the results of chemical analysis, it is evident that leaching of sulfur-containing species occurs and that this process involves also the organic moiety, not only the $-SO_3H$ group. The formation of deposits of C-containing species was also evidenced by the chemical analysis, especially for the catalyst used at 473 K. The removal of organosulfonic species and the accumulation of C-containing species take place essentially during the first reaction cycle. The subsequent catalyst uses do not result in further leaching processes or in higher accumulations of C-containing species.

3.4. Leaching process and nature of the deposits by DRIFTS studies of the used catalysts.

DRIFTS studies of the used catalysts (Fig. 3) were performed to gain information about chemical changes occurring in the catalyst under reaction conditions.

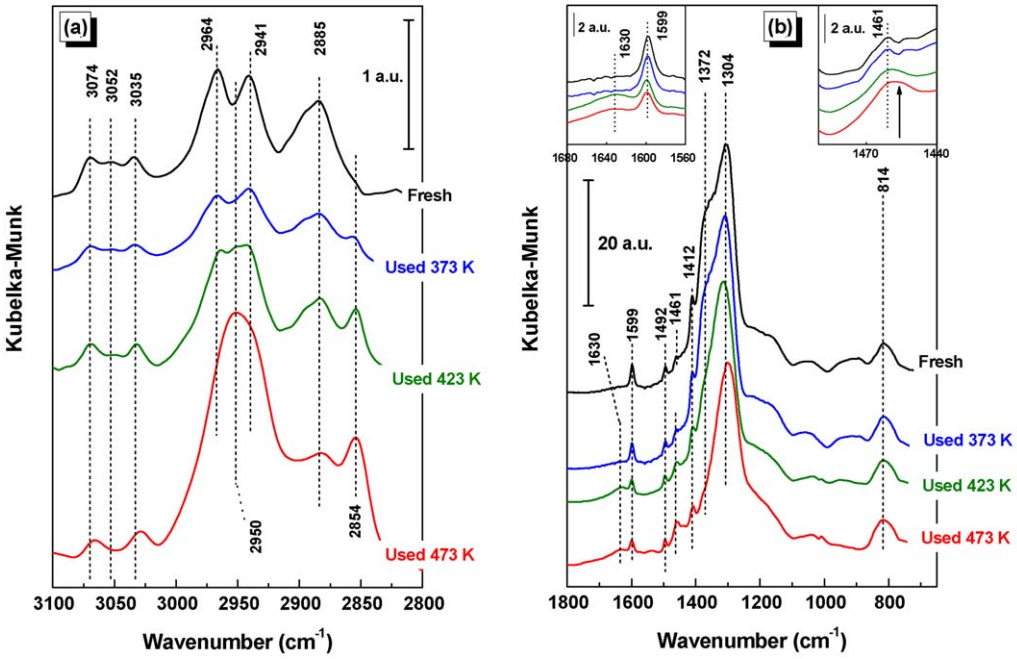

Fig. 3. DRIFT spectra recorded at 423 K of the fresh and of the used catalysts after the fourth run at 373, 423 and 473 K; (a) region 3100–2800 cm^{-1} and (b) region 1800–650 cm^{-1}.

The fresh catalyst displays IR bands of the ethyl-benzene sulfonic groups. The bands at 3074, 3052 and 3035 cm^{-1} arise from the C–H stretching vibration of the aromatic ring; the bands at 2964, 2941 and 2885 are assigned to those from the aliphatic CH_2 units. The spectral features at 1599 and 1492 cm^{-1} are assigned to the stretching of the aromatic C–C bonds, while the peak at 1461 cm^{-1} corresponds to the bending C–H mode of CH_2 methylene units of the ethyl moiety. The band at 1372 cm^{-1}, corresponding to the asymmetric S=O stretching vibration of the sulfonic group [24], appears as a shoulder of a very intense band of the SiO_2 at *ca.* 1304 cm^{-1} (stretching Si–O–Si bonds of SiO_2). Other bands of the sulfonic group, as the symmetric vibration of the S=O bond or the stretching vibration of the single S–O bond in S–O–H acid group [25], were not observed because they are weaker and overshadowed by more intense bands. The unambiguous assignation of the small band at 1412 cm^{-1} remains elusive, although it must arise from the functionalizing moieties because it is absent when the aryl sulfonic units are removed by treating the solid in air at 1073 K (spectra not shown). The band at 814 cm^{-1}, bending mode of Si–O–Si of bulk SiO_2 [26], is not significantly perturbed during reaction and does not coincide with the IR bands from the functionalization groups. This allowed us to use it as an internal reference to normalize the intensity of the other bands.

The spectra of the used catalysts display noticeable changes with respect to that of fresh catalyst. A decrease of the band at 1372 cm^{-1} assigned to sulfonic groups is clearly observed (Fig. 3b). In principle, this would indicate that the sulfonic groups are partially removed, consistent with the elemental chemical analysis results. However, the extent of sulfur removal is *ca.* 30%, and the corresponding lower intensity may not be noticeable by visual inspection. The DRIFTS experiments indicate that the decrease is more intense with the reaction temperature. Thus, the shoulder is not visible in the spectrum of the catalyst used at 473 K, inconsistent with the chemical analysis showing that irrespective of the reaction temperature, the sulfur concentration is similar in all catalysts. Therefore, the relationship between the intensity of the S=O vibration band and the concentration of sulfonic group is not straightforward. As we show later, other effects may be responsible of the lower intensity of this band.

The chemical analysis results showed that leaching does not involve the sulfonic groups only, but also affects the hydrocarbonaceous moieties. A more detailed inspection of the band at 1599 cm^{-1} assigned to C=C stretching vibration of the benzene ring (Fig. 3b; left side inset) illustrates that its intensity in the used catalyst, especially at 423 and 473 K (green and red spectra), is lower than that of the fresh catalyst. This is in agreement with the lower S content found by chemical analysis. The intensity of other C=C, C–C and C–H bands arising from the functionalizing units must also be affected in the same way, but their intensity depends also on the deposition of hydrocarbonaceous species (shown later).

A simple perusal of the C–H stretching vibrations region of the used catalysts (Fig. 3a) indicates that their IR patterns are very different to that of the fresh catalyst. The presence of two additional absorption bands at 2950 and 2854 cm^{-1} demonstrates the presence of C-containing products deposited over the catalyst surface and that they are hydrocarbonaceous species. In principle, these bands can be assigned to the stretching vibration of C–H bonds in saturated alkanes. The deposition of organic species is more intense as the reaction temperature increases. Indeed, the bands at 2950 and 2854 cm^{-1} become very intense in the catalyst used at 473 K. Additional evidence is provided by the band at 1461 cm^{-1} (Fig. 3b), originally arising from C–H bonds in methylene units of the functionalizing moiety, which is more intense and broaden in the used catalyst (upper right inset). The presence of unsaturated species deposited on the used catalysts can also be deduced from other IR features: (i) the bands at 3074 and 3035 cm^{-1} are downshifted and the band at 3052 cm^{-1} vanishes in the used catalysts that indicates that other H–C=C species are present different to that of benzene group; (ii) a band at 1630 cm^{-1} is also observed (Fig. 3b and the close up in the upper left inset) arising from stretching vibration of C=C bonds.

The DRIFT spectra of the catalyst after contact with methanol, glycerine, biodiesel, and sunflower oil at 423 K for 5 h, as well as those corresponding to the fresh and catalyst used at 423 K, are depicted in Fig. 4. The spectra of the used catalyst and that obtained after contact with methanol are similar. The coincidence of the bands arising from the organic deposits (e.g. those at 2854 and 2950 cm^{-1}) suggests that methanol is transformed in the same

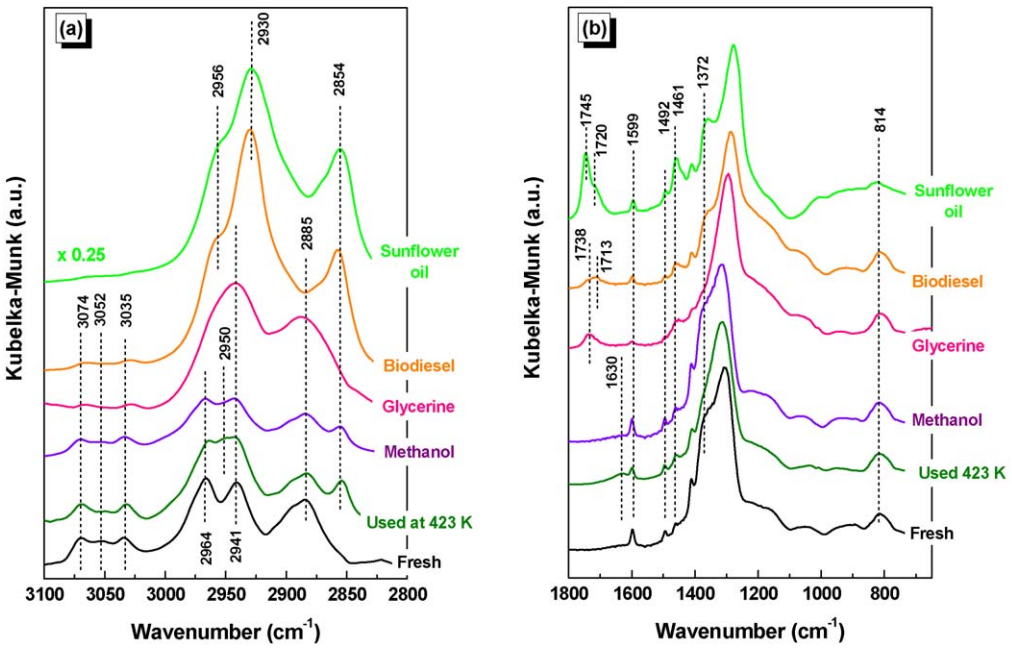

Fig. 4. DRIFT spectra recorded at 423 K obtained after contact of the fresh catalyst with methanol, biodiesel, glycerine, and sunflower oil at 423 K for 5 h; (a) region 3100–2800 cm^{-1} and (b) region 1800–650 cm^{-1}. For comparison purposes, the fresh and used catalysts after the fourth run at 423 K are also shown.

hydrocarbon species found in the used catalysts by the acid sites (like in methanol-to-gasoline (MTG) process [27]), although as shown later, this is not the case.

No discernible changes in the intensity of the band assigned to S=O vibrations (1372 cm^{-1}) are apparent in the "methanol" sample with respect to the fresh sample, although chemical analysis showed a loss of sulfur close to the 30%. This supports our hypothesis consisting in that the loss of intensity in the S=O vibration may not be due exclusively to the leaching of SO_3H groups.

The IR spectra of the catalyst contacted with glycerine at 423 K show important differences when compared to those recorded with the fresh and used catalyst. Several features indicate that functional groups are effectively leached by glycerine. Indeed, the bands appearing at 3100–3000 and 1599 cm^{-1}, used to follow the organosulfonic groups, are particularly weaker after glycerine contact (the band at 1372 cm^{-1} is very weak but, according to our hypothesis, this is not due only to the sulfur leaching). Concerning the accumulation of organic deposits in the glycerine-contacted catalyst, two bands at 2941 and 2885 cm^{-1} are now visible in the C–H stretching vibration region. These bands are consistent with the presence of glycerine-derived oligomeric species deposited on the surface [28]. Moreover, a band at 1738 cm^{-1}, assigned to the stretching vibrations of C=O bonds from carbonyl containing species is observed, presumably formed via glycerine dehydration on the acid sites [29]. This band, however, is absent in the used catalysts, meaning that they are not formed during reaction conditions. The band at 1630 cm^{-1} in the used sample is not observed either. All these results indicate that the organic deposits found in the used catalyst do not arise from the transformation of glycerine.

As in the case of glycerine, the IR spectrum of catalyst contacted with biodiesel at 423 K is different to those observed with the fresh and used catalyst. The leaching of organosulfonic species is evident in the weaker bands at 3074, 3052, 3035 and 1599 cm^{-1}. However, the effect is not as intense as that observed with glycerine, consistent also with the chemical analysis results (Table 2). Concerning the formation of organic deposits, the C–H vibration region is now dominated by three bands at 2956, 2930 and 2854 cm^{-1}, which match those found when fatty acids are chemisorbed on acid solids [30]. Two bands at 1738 and 1713 cm^{-1} are instead observed after the contact with biodiesel. None of these bands, assigned to C=O bonds from carbonyl containing species, are present in the used catalyst.

The spectra of the catalyst after contact with sunflower oil or biodiesel are rather similar. Nevertheless, a much intense accumulation of organic species occurs in the case of sunflower oil contact, evidenced by the strong C–H bands at 2956, 2930 and 2854 cm^{-1}. As explained above, these bands suggest the presence of species containing long fatty acid chains. The intense band at *ca.* 1461 cm^{-1} also evidences the presence of large deposits of species with CH_2 units. As in the case of biodiesel, the spectrum of the oil treated sample is very different to that of used catalyst. Moreover, two intense bands assigned to C=O bonds from carbonyl containing species (1745 and 1720 cm^{-1}) are observed; however, these are not present in the used catalysts. All the former results indicate that the deposits of organic species found in the used catalyst does not arise from the transformation of FAME or triglycerides catalyzed by the acid sites.

In summary, the leaching process removes the sulfonic groups and the hydrocarbonaceous moiety, as demonstrated by the lower intensity of C–H and C=C vibration bands of the organic moiety. In contrast, in our case the lower intensity of the S=O stretching band cannot be used as probe of leaching. The DRIFTS results also show the accumulation of organic species of hydrocarbonaceous nature on the used catalyst surface, consistent with chemical analysis. The contact of the catalyst with glycerine, sunflower oil, or biodiesel yields spectra different to that observed with the used catalyst indicating that the organic deposits are more complex chemically than those originated in transformation of sunflower oil, glycerine and biodiesel. The contact with methanol results in a spectrum very similar to that of used catalyst, which apparently indicates that the organic deposits arise from secondary transformations of methanol. However, the EGA-MS results (shown later) will reveal that this is not true.

3.5. Study of the organic deposits by EGA-MS studies

EGA-MS experiments were carried out to investigate the thermal stability and decomposition pattern of the hydrocarbo-

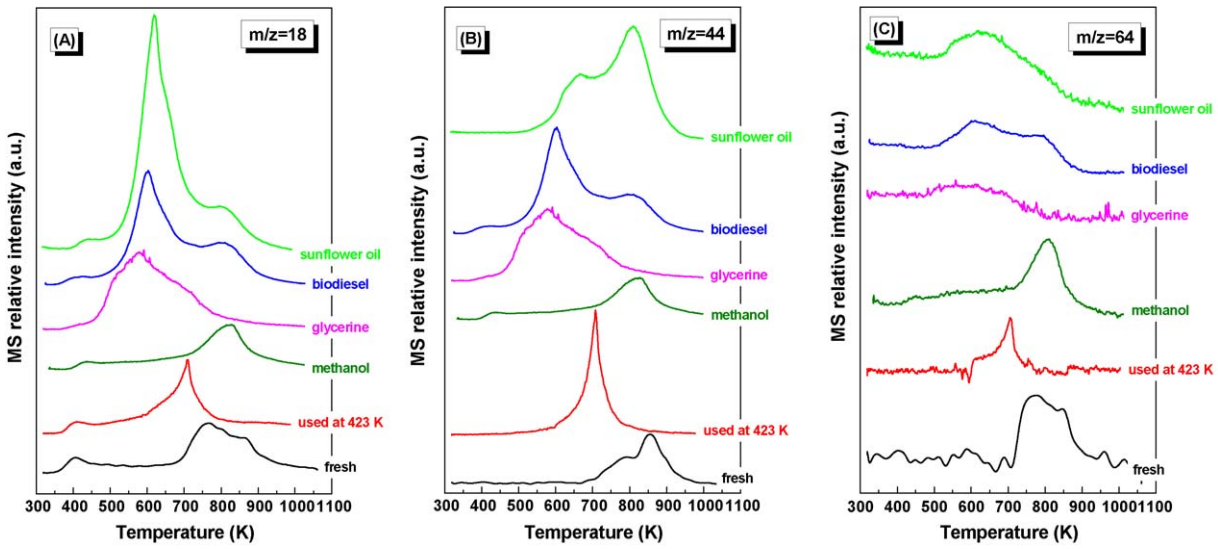

Fig. 5. EGA-MS profiles of the fresh catalyst, of the used catalyst after the fourth run at 423 K and of the fresh catalyst after contacting with methanol, biodiesel, glycerine, and sunflower oil at 423 K for 5 h: (a) fragment $m/z = 18$ (H_2O^+), (b) fragment $m/z = 44$ (CO_2^+) and (c) fragment $m/z = 64$ (SO_2^+).

naceous species accumulated on the catalyst surface. Fig. 5 depicts the evolution with temperature of the $m/z = 18$ (H_2O^+), 44 (CO_2^+) and 64 (SO_2^+) fragments obtained with the fresh catalyst, the catalyst used at 423 K (after the fourth run), as well as those with the fresh solid contacted with methanol, glycerine, biodiesel, and sunflower oil at 423 K for 5 h. The intensity of the different fragments were normalized to the $m/z = 40$ fragment (Ar^+).

The organosulfonic groups present on the surface of the fresh catalyst are combusted in the O_2-containing atmosphere between 700 and 900 K forming H_2O, CO, CO_2 and SO_2 as reaction products. The evolution pattern of CO (fragment $m/z = 28$, CO^+; not shown) was similar and as intense as that of CO_2, which indicates that CO also evolves during combustion.

The EGA-MS profile of the used catalyst is completely different to that obtained with the fresh sample. The lower area under the curve of the SO_2^+ trace is consistent with the leaching of organosulfonic groups. Furthermore, the combustion products are detected at much lower temperatures (600–800 K, with a maximum combustion rate at around 710 K). The lower area under the H_2O^+ trace indicates that the deposits present a low H/C ratio. The combustion of the hydrocarbonaceous species during the EGA-MS experiments promotes the removal of the organosulfonic groups: the deposits and the organosulfonic groups are simultaneously combusted to form H_2O, CO_x, and SO_2. This implies some kind of interaction (chemical or physical) between the sulfonic groups and the organic deposits. The simultaneous removal of H_2O/CO_2 and SO_x observed in EGA-MS experiments may also reflect the formation of local hot spots derived from the combustion of the organic deposits. However, as we will comment below, this possibility can be discarded.

Considering that polar and apolar compounds weakly adsorbed on the used catalyst were previously removed by methanol and heptane rinsing, we conclude that these organic species must be chemisorbed onto the surface acid sites rather than be physisorbed. The DRIFTS and EGA-MS studies cannot assess on whether these deposits are just covering (fouling) or poisoning the sulfonic groups, but in any case, they can be actively involved in catalyst deactivation mechanisms.

The inconsistency found concerning the lower intensity of the DRIFT S=O vibration band in the used catalysts and the chemical analysis results can be explained by accepting that an interaction between the deposited organic species and the organosulfonic groups occurs. The decreased intensity is the consequence of the interaction between sulfonic groups and chemisorbed organic deposits.

Additional support to the hypothesis that the organic species are chemisorbed on the acid sites and that the chemisorption is perturbing the S=O band is provided by the EGA-MS profiles for the $m/z = 44$ (CO_2^+) fragment for the fresh and used catalysts at 373, 423 and 473 K after the fourth run (Fig. 6). This fragment is representative of the combustion process of the organosulfonic groups and organic deposits. The profile obtained with the catalyst used at 373 K shows only a slight shifting of the combustion process and a very modest deposition of organic species. The shoulder at 700–850 K present in the fresh catalyst is not observed, and is very likely related to the leaching of organosulfonic groups noticed in the chemical analysis. On the contrary, the profiles of the

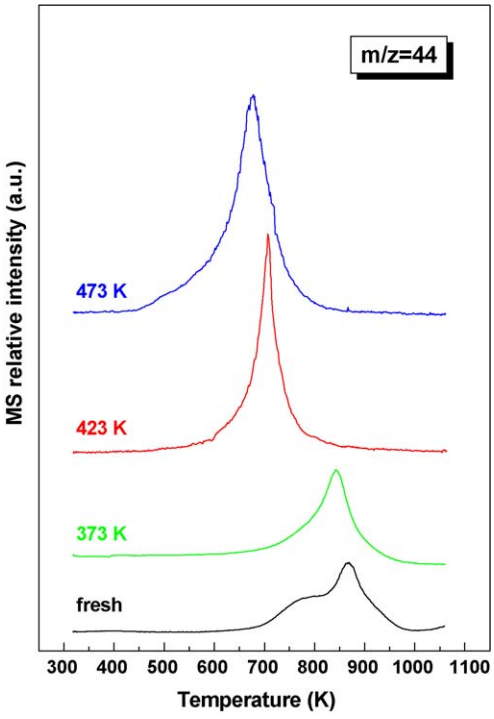

Fig. 6. EGA-MS profiles of the fragment $m/z = 44$ (CO_2^+) for the fresh and used catalysts at 373, 423, and 473 K after the fourth run.

catalysts used at 423 and 473 K (Fig. 3) show a remarkable shifting of the combustion process towards lower temperatures and an intense deposition of organic matter. These two used catalysts display a very weak S=O band (Fig. 3) although the S content is similar to that of used catalyst at 373 K. Therefore, we conclude that the organic species are chemisorbed over the acid groups and that the chemisorption is responsible of the disappearance of the S=O band by perturbing the $-SO_3H$ groups.

In an attempt to gain more information about the influence of methanol, biodiesel, oil, and glycerine on the origin of these chemisorbed organic species, the EGA-MS profiles obtained after catalyst contact with those molecules at 423 K for 5 h were also recorded. In the case of methanol contact, large differences are not found between the EGA-MS pattern of the methanol treated sample and that of the fresh sample: the evolution of CO_2, H_2O and SO_2 occurs in the same temperature range. In contrast, differences are evident with respect to the used catalyst. This indicates that although organic species can be deposited because of the methanol treatment, the interaction of these species with the sulfonic groups is rather weak. The deposits formed from methanol are, therefore, not related to those found in the used catalyst, as the DRIFT experiments apparently seemed to indicate.

The combustion process observed after catalyst contact with glycerine occurs at lower temperatures (450–800 K) when compared to that corresponding to the fresh catalyst (Fig. 5). The deposits formed from glycerine are interacting with the organosulfonic units because both are combusted simultaneously. In contrast, the combustion of the organic deposits takes place in a temperature region different to that observed with the used sample. This indicates that the organic species generated during the contact with glycerine are chemically different with respect to those found in the used catalysts. All these conclusions are consistent with our DRIFTS studies.

The catalyst contact with biodiesel results also in a combustion pattern different to that of the fresh and used catalysts. Two combustion processes are observed: the first occurs at lower temperatures (500–700 K) and is not detected in the fresh catalyst. This biodiesel-derived deposits combust simultaneously to part of the organosulfonic groups indicating that some of biodiesel-derived deposits are chemisorbed on the sulfonic groups. In the second combustion process (700–950 K) a fraction of the sulfonic groups are also combusted suggesting that some of the sulfonic groups are not affected by the organic deposits. The interaction with sunflower oil results in similar processes, although the amount of deposits is much larger than with biodiesel. Then, we conclude that the nature of the organic deposits formed by the contact with biodiesel or triglycerides is different to that found in the used catalyst.

Summarizing, the EGA-MS results confirm again the leaching of the sulfonic groups and the formation of organic deposits during the course of the reaction. These deposits are chemisorbed onto the organosulfonic acid groups. The EGA-MS profiles obtained with the catalyst contacted with methanol, biodiesel, glycerine, and oil are very different to that recorded with the used catalyst, indicating that the organic species derived from these molecules are not identical to those generated during the course of the reaction. The formation of deposits is a process more complex chemically than that occurring during the individual contact with pure reactants or products. The EGA-MS studies also show that regeneration of the used catalyst by calcination is not viable because the organosulfonic groups would also be combusted.

3.6. Leaching and organic deposits as sources of deactivation

Leaching of organosulfonic groups and the adsorption of organic species are detected in the used catalysts. The leaching phenomena lead to a lower number of active sites. It is important to notice that all the reactant and products cause leaching of active species (especially glycerine) and that leaching occurs even at low reaction temperatures (373 K). Consequently, the leaching process seems unavoidable under these operation conditions in the transesterification reaction, and may also be significant in other organosulfonic-based materials. However, leaching seems not to progress much further in the second and successive runs and therefore, its impact on the deactivation is limited. The fact that leaching does not remove all the organosulfonic groups may be explained by admitting that not all the alkyl–SiO_2 bonds show the same resistance to the leaching attack. This seems reasonable as not all the Si–OH (silanol) groups of the silica (where the alkyl sulfonic groups are bounded) display the same chemical properties.

The chemisorbed organic species are formed by side reactions involving the reactants and/or products catalysed by acid groups [31]. We also contemplate that the organic deposits may be formed from the reaction intermediates mono- and di-glycerides. This work shows, as expected, that accumulation is more significant as the reaction temperature is increased. The building-up of these deposits can occur in other organosulfonic-based materials and also in other acid catalysts. The deposition is very intense during the first run and slows down after this cycle, probably because the most active sites have been leached away or because the most active acid sites are also very active in the formation of deactivating organic species.

The results shown in Fig. 2 strongly suggest that at temperatures higher than 423 K, the adsorbed organic species participate actively in the deactivation of the catalyst. The initial reaction rate reported in this figure for the second, third and fourth cycles at 473 K are very similar to those found at 423 K. However, a higher reaction rate should be expected for the second and subsequent runs at 473 K if deposits were not present. In such hypothetical case, the reaction rate would then be defined by the concentration of the organosulfonic groups (the active acid sites) and, since all the used catalysts possess the same amount of sulfonic species, a similar ratio to that found in the first cycle between the reaction rates at 473 and 423 K should be observed for the second and successive runs. Since this is not the case, there is an additional cause of deactivation at 473 K: the organic deposits. Further support to these latter comments is provided by the Arrhenius plot for results of Fig. 2. This plot is given in Fig. 7. The results of the first cycles can be adjusted to a straight line in the whole range of temperatures. For the second run and successive runs, the reaction rates at 473 K ($1/T = 2.11 \times 10^{-3}\ K^{-1}$) are much smaller and separate from the hypothetical straight lines, which slopes are similar to that defined by the first run experiments. The reason for

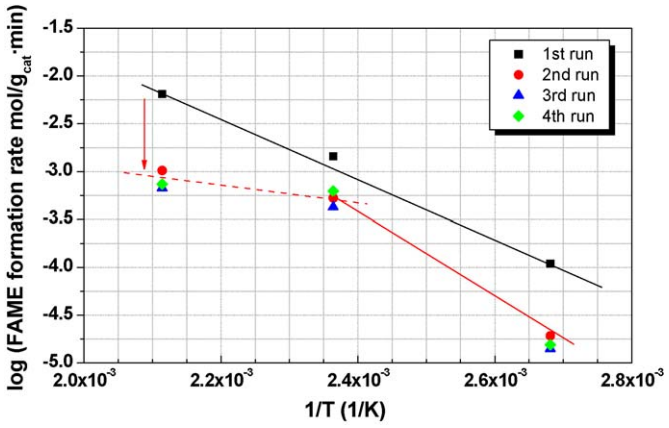

Fig. 7. Arrhenius plot of the FAME formation rate at 15 min for the different reaction cycles at different temperatures (373, 423, and 473 K).

the substantial decrease of the reaction rate and the breakthrough in the straight line at those temperatures is the deposition of organic species.

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